On the role of hydrodynamic interactions in block copolymer microphase separation

Robert D. Groot, Timothy J. Madden, and Dominic J. Tildesley

Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, L63 3JW, United Kingdom

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A melt of linear diblock copolymers \(A_nB_m\) can form a diverse range of microphase separated structures. The detailed morphology of the microstructure depends on the length of the polymer blocks \(A_n\) and \(B_m\) and their mutual solubility. In this paper, the role of hydrodynamic forces in microphase formation is studied. The microphase separation of block copolymer melts is simulated using two continuum methods: dissipative particle dynamics (DPD) and Brownian dynamics (BD). Although both methods produce the correct equilibrium distribution of polymer chains, the BD simulation does not include hydrodynamic interactions, whereas the DPD method correctly simulates the (compressible) Navier Stokes behavior of the melt. To quantify the mesophase structure, we introduce a new order parameter that goes beyond the usual local segregation parameter and is sensitive to the morphology of the system. In the DPD simulation, a melt of asymmetric block copolymers rapidly evolves towards the hexagonal structure that is predicted by mean-field theory, and that is observed in experiments. In contrast, the BD simulation remains in a metastable state consisting of interconnected tubes, and fails to reach equilibrium on a reasonable time scale. This demonstrates that the hydrodynamic forces play a critical part in the kinetics of microphase separation into the hexagonal phase. For symmetric block copolymers, hydrodynamics appears not to be crucial for the evolution. Consequently, the lamellar phase forms an order of magnitude faster than the hexagonal phase does, and thus it would be reasonable to infer a higher viscosity for the hexagonal phase than for the lamellar phase. The simulations suggest that the underlying cause of this difference is that the hexagonal phase forms via a metastable gyroid-like structure, and therefore forms via a nucleation-and-growth mechanism, whereas the lamellar phase is formed via spinodal decomposition. © 1999 American Institute of Physics.

I. INTRODUCTION

Block copolymers are polymers that consist of two chemically different sections, linked together by a chemical bond. Important examples are graft copolymers, which have a multitude of industrial applications, such as in adhesives. Here, we focus on the simpler linear diblock copolymers, consisting of two blocks linked end-to-end. Block copolymers are interesting and useful because of their tendency to form complicated aggregated structures. These structures arise because the constituents of the polymer, the \(A\) and \(B\) blocks, usually tend to segregate. The connectivity of the polymers prevents macroscopic phase separation, and consequently the system can only reduce its free energy by connecting the \(A\)-rich and \(B\)-rich domains in structures like spheres, rods, sheets, perforated sheets, or complicated sponge-like structures. The question as to which structure is formed under what condition was first theoretically studied by Leibler, who used Gaussian coil statistics to calculate the free energy in a Landau theory. The equilibrium microstructure in this theory depends on the ratio \(f\) of the length of the \(A\) section relative to the total length of the polymer, and on the mutual solubility of the \(A\) and \(B\) units, which is usually represented by the Flory–Huggins \(\chi\)-parameter.

However, experiments and Monte Carlo simulations indicate that the chain statistics are markedly non-Gaussian nearly up to the critical point. This implies that weak coupling theory cannot be used at strong and intermediate segregation. Even when the order–disorder transition is far away from the Gaussian theory prediction, the experimental structure function is still fitted successfully by the Gaussian theory. Therefore, a successful fit of the structure function is not a correct validation of the Gaussian theory. To go beyond the Gaussian approximation, self-consistent field theory has been employed which takes chain stretching into account, and fluctuation corrections to the mean-field theory have been introduced. To check these theories, simulations have been performed in which the simulated polymer size and experimental polymer size are matched. These simulations indicate that in typical experimental systems, one is indeed quite far away from the Gaussian limit, and even the best theory with fluctuation corrections does not match the simulation results completely.

The transition of a copolymer system from one mesophase structure into another is an important process which has recently become a subject of theoretical study. Techniques used are dynamical Landau theory, and self-consistent field theory from which the kinetic pathway can be inferred or actually calculated by representing the local polymer density in the unit cell with a large set or orthogonal functions. Another approach is the Monte Carlo...
It is based on 27 different systems and should therefore only have an alternative method to simulate the dynamics of mesophase formation. The method that we propose here is the dissipative particle dynamics (DPD) method, which is a continuum simulation technique of polymer chains in three dimensions, which correctly represents all hydrodynamic interactions. Another advantage of this method is that any mixture of polymers can be simulated, where the polymers can have an arbitrary loop-or branching structure. Without changing the software or increasing CPU time, we can simulate a blend with thousands of different chemical species. However, since most experiments and theory are done for simple linear diblocks, we used these as a benchmark for the method.

To gain confidence in this simulation technique, we briefly review previous work that mainly concentrated on validating the method by its predicted equilibrium structures, though some indications on the various pathways by which equilibrium is reached were given.

A schematic phase diagram obtained from these simulations is shown in Fig. 1. The “effective” Flory–Huggins parameter is obtained by extrapolation to infinitely long chains, using finite chain simulations. We arrived at this diagram by modifying the theoretical phase diagram as predicted by Matsen and Bates. It is based on 27 different systems and should therefore only be seen as a rough indication of where we find which phase. Our diagram compares well to the diagram that Larson produced for short lattice chains in a monomer solvent. In accordance with mean-field theory, the simulated diagram shows the classical quasi-solid body-centered cubic (BCC), hexagonal (H), and lamellar phases (L). However, we also find melted structures like a micellar phase (M), a liquid rod phase (LR), and a connected tube phase (CT). These melted structures agree with experimental observation, and with Monte Carlo simulations of block copolymers. A liquid-like phase of interacting micelles between the disordered phase and the hexagonal and lamellar phases has also been found from the rheology and small-angle x-ray scattering (SAXS) data of concentrated solutions of block copolymers. We also find a hexagonally perforated lamellar phase (HPL) that is observed in experiments, and a small region where screw dislocations in a lamellar phase are stabilized (SDL), although the stability of the HPL phase has been debated. As in all simulation methods, the finite system size may lead to artificial preference of one phase over the other. However, in terms of the number of microdomains in the simulation box, our systems are larger than any of the previous Monte Carlo simulations.

To introduce the formation process of the mesophases, we briefly repeat the qualitative findings from DPD simulations that have been reported elsewhere. Processes on three different length- and time scales can be distinguished in the formation of polymer microphases: (1) phase separation on the mesoscopic bead level, (2) organization of polymers into micelles, and (3) the organization of these micelles into a superstructure with its own particular symmetry. A schematic diagram summarizing the different effects is shown in Fig. 2. The evidence for this scheme comes from observing the time evolution of polymer systems of various composition at a fixed value of $\chi N$, and capturing the qualitative effects of the evolution in a simple picture. This is a conceptual framework, which helps to rationalize the evolution, rather than an exact description of the location of various transition points. These will obviously depend on the precise value of $\chi N$. Effects on different length scales interplay in
both the final structure and in the pathway to form it. On level 2, the symmetry of the micelles (spherical, rod-like, or planar) is the dominating factor. The transitions between these structures at the particular AB segregation parameter used in these simulations (roughly $X^{0.4N\approx 20}$ for $N\to\infty$) are $f_1 \approx 0.20$ and $f_2 \approx 0.37$. On a global level (level 3), the important transition points are the percolation transition, where the rods form a interconnected tube network, the nematic transition, and the smectic transition. These are located, respectively, at $f_{p1} \approx 0.23$, $f_{p2} \approx 0.27$, and $f_{p3} \approx 0.32$. For compositions where $f_{p1} < f < f_{p2}$, a percolating interconnected tube phase is formed as a precursor of the final phase. Experimental evidence comes from time-resolved x-ray scattering; see Balsara et al.\textsuperscript{24} and references therein. These experiments reveal the presence of two processes, a fast process that is believed to be related to the local segregation of the blocks (ordering levels 1 and 2) and a slow process that leads to long-ranged order (level 3).

Now we turn our attention to the role of hydrodynamic interactions. The importance of hydrodynamics in macroscopic phase separation is well established,\textsuperscript{25} but in particular for AB structures at the particular levels where $f_{p1} < f < f_{p2}$, a percolating interconnected tube phase is formed as a precursor of the final phase. Experimental evidence comes from time-resolved x-ray scattering; see Balsara et al.\textsuperscript{24} and references therein. These experiments reveal the presence of two processes, a fast process that is believed to be related to the local segregation of the blocks (ordering levels 1 and 2) and a slow process that leads to long-ranged order (level 3).

For ordering of block copolymers, this would imply that there is some crossover point beyond which hydrodynamic interactions are dominant. One way of establishing this crossover point is to study the process in a numerical simulation, and study the influence of the presence or absence of hydrodynamic interactions. For a symmetric polymer, a lattice-based dynamic self-consistent field (SCF) simulation without hydrodynamic interactions fails to produce the (correct) lamellar equilibrium structure irrespective of the simulation time.\textsuperscript{16} For this reason, we previously hypothesized that hydrodynamic interaction plays a key role in the formation of a mesophase. The problem with this approach is that two different techniques are compared, a lattice method and a continuum method. A difference in the results therefore does not provide a clear indication of the role of hydrodynamics, separate from lattice artifacts and the nonlocality of the Onsager kinetic coefficient.

A clearer comparison to establish the role of hydrodynamic interactions can be made when simulations are performed with and without hydrodynamics included in the same method. Within the SCF method, this approach was taken by Maurits et al.\textsuperscript{27} who conclude that without externally applied shear the separation process in the latter stages of evolution proceeds faster when hydrodynamics is present, as compared to a purely diffusive model. However, even though the free energy converges faster to a limiting value, the isosurfaces, representing the structure with and without inclusion of hydrodynamics show very little difference, see Fig. 3 of Ref. 27. In both cases, the SCF approach does not converge to a lamellar phase for a symmetric block copolymer, whereas the DPD method does. Technically speaking, the SCF method is formulated as a continuum theory, and the free energy can be minimized by representing the density via any set of (orthogonal) basis functions. In practice, however, the dynamic SCF equations are solved on a lattice,\textsuperscript{16,27} and when the interface width becomes comparable to the size of the lattice spacing (at intermediate and strong coupling), lattice artifacts may arise.

To resolve this problem, we have compared two continuum simulation methods. Both describe the same Hamiltonian system, but they differ in their evolution algorithm. The first method is the dissipative particle dynamics method, and the second is the Brownian dynamics method. The only difference between the two is that all hydrodynamic interactions are taken into account in the former method, but they are completely absent in the latter method. The polymer architecture, connectivity, interactions, and the liquid compressibility are explicit in both methods. Thus, we can make a very pure comparison to see what happens if only hydrodynamics is turned off while all other physical effects are included. This puts us in the position to compare results from four different simulation approaches: the (lattice) SCF method with and without hydrodynamics, and a (continuum) soft-sphere model with and without hydrodynamics. For symmetric polymers, the soft-sphere model is found to predict the formation of lamellar domains of some eight lamel-
lae across, irrespective of the presence of hydrodynamic interactions. The SCF method does not develop such a layered structure without the application of shear, irrespective of the inclusion of hydrodynamics. To assess the merits of both models, their predictions have been compared with experiments in Sec. IV. Without external shear, experimental samples remain globally disordered, but local order does appear spontaneously. The experimental systems that we are aware of form domains of some eight lamellae across; hence, they order on the length scale seen in the DPD simulations.

It should be noted again that, to reach ordering at large length scales, one has to pass a mesoscopic ordering process into local domains, denoted by “level 3 ordering” in Fig. 2. The formation of these structures clearly depends on what happens at level 2, which involves differences in local structure. An important question, therefore, is whether hydrodynamic interactions are equally important for all pathways towards the equilibrium state, or if its importance depends on the intermediate structure that is formed. For this reason, we studied both the evolution of symmetric copolymers and of asymmetric copolymers. In the next section, we describe the simulation model and methods in detail, and discuss the applicability to polymer systems. In Sec. III we describe the simulation results. These are discussed and interpreted in Sec. IV, where we also speculate on the consequences of our results, and compare them to existing experimental observations. The conclusions that we can draw unambiguously are summarized in Sec. V.

II. SIMULATION MODEL AND METHODS

In the present coarse-grained or mesoscale simulations, a polymer chain is represented by a set of beads connected by springs. Each bead represents a section of the polymer chain corresponding in size to the persistence length of the polymer. The atomistic details of the polymer are sacrificed so that we can evolve the coarse-grained system on a sufficiently long time scale to study the formation of microstructures. A simple model of a linear block copolymer is formed by joining polymers of the same type and fomers. A simple model of a linear block copolymer is formed by using the modified Verlet algorithm introduced by Groot and Warren33 to integrate the equations of motion. In this method, the temperature is controlled by adding a drag force and a random force to every particle; these forces act relative to a fixed background. The drag force and the random force act as heat sink and source, respectively, so that they combine to form a thermostat. They are given by

\[ F_i^d = \sigma \xi_i / \sqrt{d \Delta t}, \quad F_i^p = -\gamma \vec{v}_i, \]

where \( \sigma \) and \( \gamma \) are the noise and friction coefficients, \( \xi \) is a random vector of variance \( \lambda \) in each direction, and \( d \Delta t \) is the timestep used. This thermostat leads to the equilibrium temperature, \( k_B T = \sigma^2 / (2 \gamma) \). The problem with this method is that it does not conserve Newton’s third law, because some randomness is added to the conservative forces. The consequence is that the acceleration of a fluid element is not given exactly by the sum of all forces exerted on its boundary. Since this condition forms the basis of the Navier–Stokes equation, this Brownian dynamics method does not conserve hydrodynamic interactions.

In the DPD method, noise and friction are also included, but these forces are calculated for pairs of neighboring particles.34 The noise and drag forces, respectively, are given by

\[ F_i^\xi = \sigma \sum_j \omega(r_{ij}) \vec{r}_{ij} \xi_{ij} / \sqrt{d \Delta t}; \]

\[ F_i^\gamma = -\frac{1}{2} \sigma^2 / kT \sum_j \omega(r_{ij}) \left( \vec{v}_{ij} \cdot \vec{r}_{ij} \right) \xi_{ij}, \]

where \( \xi_{ij} \) is a random variable with zero mean and variance \( \lambda \) for each pair \((i,j)\) of particles, and \( \omega(r) \) is a weight function for which the functional form of Eq. (2) is used. Because the DPD method satisfies Newton’s third law, the acceleration of any fluid element is given exactly by the sum of all forces that act on its boundary. Consequently, this method leads to a correct description of hydrodynamics.36 Hence, even though the forces only act locally, the simulations include long-range velocity correlations. The friction factors in the DPD and the BD simulations have been chosen such that the bead diffusion constant in a fluid of single beads is the same in both methods: \( \sigma = 3; D_{\text{bd}} = 0.3 R_c^2 / \tau \).

Both in the BD simulations and in the DPD simulations, we used the modified Verlet algorithm introduced by Groot and Warren33 to integrate the equations of motion. In this method, the velocity that is used to calculate the friction between two time steps is taken at a well-chosen point in the interval between \( t \) and \( t + \Delta t \), such that the errors are minimized, i.e.,

\[ r_i(t + \Delta t) = r_i(t) + \Delta t \vec{v}_i(t) + \frac{1}{2} \Delta t^2 f_i(t) \]

\[ \vec{v}_i(t + \Delta t) = \vec{v}_i(t) + \lambda \Delta t f_i(t) \]

\[ f_i(t + \Delta t) = f_i(r_i(t + \Delta t), \vec{v}_i(t + \Delta t)) \]

\[ \vec{v}_i(t + \Delta t) = \vec{v}_i(t) + \frac{1}{2} \Delta t f_i(r_i(t + \Delta t); f_i(t + \Delta t)), \]

where \( \lambda = 0.65 \) is taken. This value allows for a time step \( \Delta t = 0.06 \) without any sacrifice in accuracy. If we aim for temperature \( T = 1 \), the simulation in reality converges to temperature \( T = 1.015 \) with a mean fluctuation amplitude \( \Delta T \)
III. SIMULATION RESULTS

Since different compositions lead to aggregates of different topology, it is not clear if the influence of hydrodynamic interactions are equally important in the different regions of the phase diagram. For this reason, we have performed simulations both for asymmetric polymers \( f = 0.3 \), where the system has to go through a percolated state and a nematic transition to find its equilibrium structure (see Fig. 2), and for symmetric polymers \( f = 0.5 \), where domains of local lamellar order have to grow together to form a macroscopically homogeneous phase. We first present the results obtained for an A₁B₇ copolymer, which forms an example of the former route to equilibrium. The simulations were performed in a box of \( V = 20 \times 20 \times 20 \) using periodic boundary conditions. At time \( t = 0 \), 2400 copolymers of structure A₁B₇ were arranged randomly in the box and the systems were allowed to evolve. The evolution of the microstructure is monitored by calculating the \( AB \) dividing surface as a function of time. This surface is defined as the surface of equal A and B density and it highlights the mesophase structure of the system.

Figure 4 shows three stages in the evolution of the simulated systems. The DPD simulation quickly forms microphase separated regions that percolate into interconnected tubes. These tubes form a globally disordered fluid phase with tubes changing shape and moving relative to each other. After approximately 7500 \( \tau \) a domain of hexagonal order is formed, which grows out at the expense of the disordered phase. The subsequently formed hexagonal phase is stable for the remainder of the simulation. On the basis of self-consistent field calculations, it has recently been put forward^{12} that the hexagonal phase is formed from the gyroid by a process where first fivefold connection points are formed, that subsequently break into a threefold connection and two unconnected tubes. We do not find evidence of this mechanism in our simulations. Instead we find only three- and fourfold connection points, linked by short liquid bridges
that sever by a necking mechanism. In the last stages of evolution, where the sample is almost completely hexagonally ordered, we find local defects in the form of liquid bridges between otherwise parallel rods. The dominant mechanism for topological transitions in that stage is the rupturing of these liquid bridges; see the top-right picture in Fig. 4.

The path taken by the BD simulation is very similar to that of the of the DPD simulation in its early stages: the formation of a phase of interconnected tubes. Also, in the BD simulation we find the tubes locally align in a hexagonal structure, but this phase is subsequently destroyed again. In many places throughout the simulation box, small hexagonal domains arise and disappear. None of these domains manages to grow out to a globally ordered hexagonal phase, even when the simulation is extended to 24 000 $\tau$. One may argue that there could be a subtle bug in the BD program, which makes the hexagonal phase unstable. If that were the case, then it is obvious that the hexagonal phase does not form in the BD simulation. To check this loophole, the hexagonal structure as generated by the DPD simulation was used as a starting configuration and was evolved in a BD simulation over 50 000 time steps (3000 $\tau$). The hexagonal phase remained stable. In fact, the shape fluctuations of the tubes are smaller than they are in the DPD simulation. So either the hexagonal phase is metastable but the BD method cannot break it apart, or it is stable and the BD method cannot form it. In either case, it is demonstrated that there is a kinetic barrier that the BD method cannot cross. Since the DPD method can cross this barrier, and since the only difference between the two simulation methods is the conservation of momentum leading to a correct description of hydrodynamics in the DPD method, we conclude that hydrodynamic interactions are important to cross this barrier.

To quantify the order in the system, a simulation box can be divided into small cells. In each cell, the local density of $A$-beads is determined, and the order parameter

$$\omega = \frac{1}{V} \int_V \left( \frac{\rho_A(r)}{\rho} \right)^2 - f^2 d^3 r \propto \sum_{k \neq 0} \rho_A(k) \rho_A(-k), \tag{7}$$

or small variations thereof has been defined in the literature. In a completely disordered system this parameter vanishes. Nonzero values of this order parameter indicate local segregation, i.e., the order parameter measures whether the $A$ and $B$ beads are demixed on a local scale. Though this is a perfectly valid measure of segregation, it is insensitive to the way in which segregation has taken place. In a homopolymer mixture, in the strong segregation limit, this parameter would have the same value if there are $A$ domains in a $B$ matrix or if macroscopic phase separation would have taken place. Consequently, this order parameter does not distinguish between ordering on the various length scales (levels 1, 2, and 3 in Fig. 2). To define a more descriptive order parameter, we start at the right-hand side of Eq. (7), and first calculate the full 3D structure function

$$S(k) = \rho_A(k) \rho_A(-k)/N_A,$$  

where $N_A$ is the number of $A$-particles in the simulation. This function is the most natural representation of the structure.

The sum over all $k$-modes renders the order parameter $\omega$ again, but before we define an order parameter we first concentrate on the full 3D structure function. Its time evolution for the DPD system is shown in Fig. 5(a). What we observe happening is that the system in Fourier space first peaks in a spherical shell around the origin (top left). This already corresponds with level 2 ordering (see Fig. 2) as the real-space structure (shown top left in Fig. 3) is a network of tubes; level 1 ordering takes place on a much shorter time scale. When level 3 ordering sets in ($t \approx 7500$), the spherical symmetry is broken, and a ring structure emerges. In real space, this ring corresponds to a hexagonal domain embedded in a network of tubes; see the top-middle structure in Fig. 4. This ring subsequently breaks in two halves, that thereof on each break up into three peaks. The spherically averaged structure function is shown in Fig. 5(b). The dashed curve is the structure function at $t = 1500$, and the full curve is the result at $t = 15 000$. Note that the latter curve shows a peak at $k = \sqrt{3} k_{\text{max}}$, which is characteristic for the hexagonal phase, and that the main peak has narrowed considerably, indicating increased order.

A very similar spherically averaged structure function was reported in experiments; see Fig. 2 of Balasara et al. 24

![Schematics of simulations](image-url)

**FIG. 5.** (a) Fourier representation of the sequence of events to form a hexagonal phase (bottom right) from an isotropically disordered system (top left), for an $A_B$ block copolymer simulation with hydrodynamics. (b) Spherically averaged structure function of the $A_B$ DPD simulation, for times $t = 1500$ (dashed curve) and $t = 15 000$ (full curve). Note that the latter shows a characteristic secondary peak near $k = \sqrt{3} k_{\text{max}}$.  
The time dependence of the structure function demonstrates that the ordering mechanism goes through various stages, where fewer and fewer modes contribute to the structure. It is this decreasing number of modes contributing to \( S(k) \) that is characteristic for the increasing amount of order. Therefore, we would like to count the number of \( k \)-vectors that contribute to the structure. Since \( S(k) \) can be interpreted as a density of states in Fourier space, we now define the order parameter by analogy to the entropy of particles distributed in real space as

\[
P = \int S(k) \ln S(k) d^3k.
\]  

(9)

This parameter has properties related to the configurational entropy of the structure. In a completely disordered system, \( P = 0 \), and when a system orders, it increases. Because it is a nonlinear functional of the structure function, it distinguishes between systems with a different number of peaks that have the same overall segregation \( \omega \).

In Fig. 6 this order parameter is shown for the DPD simulation (with hydrodynamics) and for the BD simulation (without hydrodynamics). The \( A_3B_7 \) simulation results are marked HEX. Whereas the DPD simulation shows a continuous increase in order (i.e., self-structuring of the system), the other simulation shows no clear trend. The behavior of the order parameter demonstrates that hydrodynamic interactions are essential in driving this system to the structure of lowest free energy, for this particular point in composition space.

Now we turn our attention to the formation of the lamellar phase. Again, we performed DPD and BD simulations of 2400 polymers in a box of size \( V = 20 \times 20 \times 20 \) using the normal periodic boundary conditions, but now we studied a melt of \( A_3B_5 \) block copolymers. As reported previously,\(^{16} \) the DPD simulation swiftly finds its lamellar equilibrium structure. In light of the previous observations, one might expect that the BD simulation does not find the correct equilibrium, because hydrodynamic interactions are absent here. However, the BD simulation does converge to the correct equilibrium, following exactly the same dynamics as the DPD system does. Both with and without hydrodynamics, the system orders into a single lamellar domain; hence, hydrodynamics is not essential for the formation of a lamellar phase. The increase of the order parameter in these simulations is shown in Fig. 6; the curves are marked LAM. Note that the time scale of evolution here is much shorter than for asymmetric polymers (marked HEX), where a connected tube structure is formed in the second stage of evolution. The time to form the hexagonal phase is about a factor of 8 larger than the time to form the lamellar phase.

To study finite size effects (a small simulation box may help to induce ordering), some extra simulations were run in a larger box (\( V = 30 \times 30 \times 30 \)). The relevant parameter that defines the system size is the box size divided by the lamellar or hexagonal spacing. For this reason we also use smaller polymers: \( A_1B_3 \) and \( A_2B_5 \). In these runs, 20 250 polymers were simulated. This extra coarse graining naturally sacrifices details of the structure, but it allows us to investigate the evolution of the structure on larger length- and time scales.

To compensate for the smaller polymer length, the repulsion between the \( A \)-beads and the \( B \)-beads was increased so that \( \chi N = 40 \) in the \( A_2B_5 \) simulations (repulsion parameter between particles of different type is \( f_{\text{max}} = 57.7 \)), and two values of \( f_{\text{max}} \) were used in the \( A_1B_3 \) simulations: \( f_{\text{max}} = 57.7 \) and \( f_{\text{max}} = 80.4 \). The latter value compensates for the increased fluctuation correction of a shorter chain.\(^{16} \) \( \chi^{\text{eff}} N = \chi N / (1 + 3.9 N^{3/2}/2^{23/2} v) \) is taken constant, where \( v = 0.65 \).


±0.02 was obtained for the $A_3B_7$ system far away from the critical point, using Eq. (6).

Three stages of the evolution of this system, obtained using the BD technique, are shown in Fig. 7. These three conformations are illustrative of the ordering on various length scales that we denoted by levels 1, 2, and 3 in Fig. 2. Note that the organization on level 2 does not resemble the connected tube structure shown in Fig. 4. It is qualitatively different. The growth of the order parameter in the $A_2B_2$ systems is shown in Fig. 8. Both systems clearly evolve towards the lamellar state, but do not reach a completely uniform lamellar state. In this, the DPD and BD results are very comparable to each other and to what is found in experiments (see Sec. IV). What prevents these systems from reaching a uniform lamellar state is the presence of two screw dislocations that cross the periodic boundary conditions four times. These screw dislocations appear as a consequence of the mismatch between two large lamellar domains of different orientation. This apparently leads to too high a kinetic barrier to cross. Since BD and DPD lead to the same result, we must conclude that hydrodynamic interactions are not crucial when the level 2 organization is in the lamellar state. The formation of these layers is therefore diffusion limited.

Finally, we discuss the DPD simulation of 20 250 $A_1B_3$ polymers in the $30 \times 30 \times 30$ box. A conformation at time $t = 3600 \tau$ for the system with $AB$ repulsion $f_{\text{max}} = 80.4$ is shown in Fig. 9. This system is disordered on a global level, though locally hexagonal order persists over domains of some four tubes across. Beyond this length scale, the growth of the hexagonal domains stops. The hexagonal domains that are formed in this simulation are observed to be quite stable. In that respect, this system is different from the $A_3B_7$ BD simulation shown in Fig. 4. In that simulation, very small domains of hexagonal ordering appear, but are subsequently destroyed again. Here, the hexagonal domains are not local fluctuations, but behave as stable “droplets” of hexagonal phase that keep moving around. The comparison with the $A_3B_7$ simulations can only be done qualitatively, as these polymers are much shorter and have a different composition.

However, in the phase-separated $A_3B_7$ system we have an endpoint separation $R_e = 3.43 \pm 0.08$ and a diffusion constant $D = 0.014 \pm 0.001$, whereas in the $A_1B_3$ system these are $R_e = 2.03 \pm 0.01$ and $D = 0.028 \pm 0.003$. Hence, the Rouse time for the short polymer is shorter by a factor of 5.6 ± 0.5. This implies that time 3600 in this system corresponds to time 20 000 ± 2000 in the $A_3B_7$ system.

IV. DISCUSSION

Here, we present the results of two simulation methods for the evolution of block copolymer melts, differing only in the presence or absence of hydrodynamics in the simulation method. These two methods are specifically chosen to minimize any other differences in the model and the algorithm. For asymmetric copolymers, the DPD simulation, which includes hydrodynamics, produces the hexagonal phase predicted by theory and other simulation studies. However, the Brownian dynamics simulation, which does not include hydrodynamics, does not produce the expected phase but remains trapped in an intermediate structure of interconnected tubes. From these results, we conclude that hydrodynamics is important in driving the kinetics of microphase separation when an interconnected tube phase is formed as an intermediate structure. This intermediate structure is formed as a precursor for the hexagonal phase and the perforated lamellar phase. Indeed, in the formation of the HPL structure, we found a similar slow evolution as in the formation of the hexagonal phase. The result presented here is a typical example; we have found a very similar pathway and slow evolution in other points within the hexagonal and HPL phases.

For symmetric block copolymers that evolve along a pathway which avoids the intermediate connected tube structure, the system evolves quite efficiently if no hydrodynamic interactions are included. Hence, hydrodynamic interactions are not critical in this case. The observed mechanism for microphase separation is one of the simultaneous formation of domains of lamellar order throughout the box. These domains seem to grow faster in the direction perpendicular to the lamellae than parallel to them.

Before giving our interpretation of this result, we first discuss the possible role of finite size effects. In Monte Carlo simulations...
simulations of asymmetric block copolymers, hexagonal ordering is also obtained even though hydrodynamic interactions were not taken into account, but these systems contained only a few hexagonal rods. It is very conceivable that finite size effects helped establishing the ordered phase in those simulations. In terms of the number of hexagonal spacings our systems are larger, but the key question is: are our systems large enough? To answer this question, we recall that the BD and DPD methods simulate the same Hamiltonian system, and that both generate the correct Gibbs–Boltzmann distribution. Deviations from the equilibrium (single bead liquid) pair correlation are negligible. Nevertheless, the DPD system orders completely, whereas the BD system does not. If the box size were intrinsically too small, i.e., small compared to the correlation length in the disordered tube state, then the BD system would also be forced into the ordered state. The fact that the simulations are locked in once a completely ordered state is reached is obviously a finite size effect: then the correlation length exceeds the system size. This, however, does not mean that the simulated pathway towards this state is incorrect; during the evolution towards the ordered state the correlation length is shorter than the system size. Finally, in our $A_1B_2$ simulation in a larger box, we find hexagonal domains of some four rods across. This implies that the $A_1B_2$ box is of the right size to represent a single hexagonal domain. For these reasons we are confident that our results of the dynamical pathway to form the hexagonal phase are realistic.

To interpret these results, we first rule out that the onset of nematic ordering requires long-range correlations. The dynamics of the isotropic–nematic transition for simple hard platelets and rods does not require hydrodynamic interactions, as Monte Carlo simulations without momentum conservation efficiently produce a nematic state. In fact, our BD simulations also produce small ordered domains, but these domains don’t grow out to a single macroscopic ordered state.

Two observations are of key importance for our interpretation. First, we observe that an ordered domain arises locally from a disordered system, and then grows out at the expense of the disordered phase. In the larger simulation box we find several domains of hexagonal symmetry to arise and grow out. These are direct observations of the nucleation-and-growth mechanism to form the hexagonal phase. The second observation is that in the formation process towards the hexagonal phase, hydrodynamic interactions are of dominant importance. The analogy to ordinary phase separation in a binary mixture now implies that the domain’s size must grow linear in time, see Eq. (1). A theory predicting a linear growth law has been formulated by Goveas and Milner, who took the nucleation-and-growth mechanism as a starting point. This theory has recently been tested by experiment. The front velocity by which the ordered domain is theoretically predicted to grow matches the experimental observation without adjustable parameters. This indicates first that the ordering mechanism into the hexagonal phase does indeed proceed via a nucleation-and-growth mechanism, as in the present simulations, and second, it affirms a linear growth law for the domain, which in turn indicates that the process is dominated by hydrodynamic interactions. In fact, Frederickson and Helfand’s theory that accounts for fluctuation corrections predicts that the spinodal is suppressed to $T = 0$, which implies that the ordering process should always occur via nucleation and growth, irrespective of the quench depth.

So why does this mechanism not apply to the formation of the lamellar phase? A mathematical argument is that the nature of the symmetry change between isotropic and hexagonal requires the transition to be first order: the Landau expansion contains a nonzero cubic coefficient. This is not the case for the isotropic to lamellar transition, which (in the Landau expansion) is second order, but becomes weakly first order when fluctuations are taken into account. Hence, there is a natural tendency for a nucleated process in the former transition, whereas this is not the case in the latter. The isotropic to lamellar transition therefore must be spinodal. To explain this in a heuristic way, we first remark that if the disordered phase is unstable with respect to the ordered phase, the transition occurs by spinodal decomposition, as there is no barrier to overcome. Nucleation and growth can be expected when the disordered phase is metastable, because a free-energy barrier then separates the two phases. Now, the hexagonal phase arises from a disordered network of tubes. We speculate that this phase is metastable because it resembles the gyroid structure (one might refer to it as a melted gyroid phase), and because of the previous symmetry argument. This implies a (strong) first-order transition; hence, the hexagonal phase can be expected to grow via a nucleation-and-growth mechanism. The lamellar phase is formed from a structure of disordered lamellae, which is topologically different from the gyroid phase. There is no stable phase that resembles the disordered lamellar system. Therefore, this structure is unstable with respect to the lamellar phase (i.e., the isotropic to lamellar transition is second order or weakly first order), and thus the lamellar phase must form via a spinodal growth law.

This difference in the pertinent growth mechanism is reflected in the increase of the order parameter over time. Figure 6 demonstrates that the lamellar structure is formed directly, while the hexagonal phase is formed after a certain delay time, because the structure lags in a metastable state. This behavior is very similar to what is seen in the experiment, at least in a limited temperature range; see, e.g., Fig. 3(a) of Balsara et al. Their observed spherically averaged structure function (Fig. 2 of Ref. 24) is quite similar to our Fig. 5(b). Other experiments on the formation of the hexagonal structure involve SAXS and rheology on polystyrene/polyisoprene block copolymers by Hashimoto et al. These authors find a structure function similar to our Fig. 5(a), and they also find clear evidence that after a quench below the order–disorder temperature, the ordering into the hexagonal phase occurs via a nucleation-and-growth process. This seems at variance with the predictions of Leibler’s theory, predicting first the formation of spherical microdomains that subsequently form a hexagonal phase. Other SAXS observations of the ordering from a gyroid phase into the hexagonal phase show exactly what we have found in the present simulations [see Fig. 5(a)]. Almdal et al. state that
in the absence of shear, no macroscopic hexagonal ordering is obtained; instead, they assert the formation of domains of different orientation. This corresponds well with what we find in our larger simulation system; see Fig. 9. By shearing the sample, Almdal et al. find the domains to order on a macroscopic scale. Again, the sequence they find for the scattering pattern exactly matches our simulation result, shown in Fig. 5(a).

An important point of discussion is the low viscosity in DPD simulations, and the amount of order that is found without shearing the system. The dimensionless quantity that is relevant here is the Schmidt number, $Sc = \nu / D$, which was studied by Groot and Warren for DPD liquids of single beads. For a melt of homopolymers of length 10 and the present noise and friction parameters, the viscosity is obtained as $\nu = \eta / \rho = 1.87 \pm 0.13$ whereas the diffusion constant is $D = 0.0336 \pm 0.0001$, hence the Schmidt number is $Sc = 56 \pm 4$. For block copolymers, we have no estimate of the viscosity, but the diffusion constant in the $A_3B_7$ system is $D = 0.0142 \pm 0.0001$. Assuming that the viscosity must have gone up relative to the homopolymer by at least the amount that the diffusion constant went down, we find a lower bound for the Schmidt number as $Sc > 310 \pm 20$. Whether this is large enough to represent a real copolymer system can best be assessed by comparing the simulations to electron micrographs of spontaneously ordered systems. Such studies reveal that the typical size of a lamellar macro domain in a casted film is at least eight lamellae, but the directional order can extend over much larger length scales.

The influence of shear on the microstructure is highlighted by Winey et al., who find that an oscillatory strain by 5% is already enough to induce complete lamellar ordering. Their TEM results for an unstrained system also shows domains of the order 10 bilayers. The size of the domains found in experiments corresponds well to the domains as in Fig. 7. The simulated domains do not grow out to fill the whole box, but rather, two macro domains arise containing some seven independent lamellae. This suggests that on a larger length scale the simulated system would be isotropic. However, to observe this behavior explicitly in a simulation would require a much larger simulation box, containing some $10^6$ particles. This is well within reach if a parallel code is used on a super computer.

Finally, we discuss the consequences of the fact that the lamellar phase is formed nearly an order of magnitude faster than the hexagonal phase. From this large difference in evolution rate, we infer the viscosity of the hexagonal phase to be much higher than that of the lamellar phase. This can be understood as follows. In general, the viscosity is determined by the time integral over the stress–stress autocorrelation function; see, e.g., Groot and Agterof and references therein: $\eta = \frac{V}{2kT} \int_0^\infty \sigma(0) \sigma(t) dt$. In practical terms, this can be reduced to

$$\eta = G \tau,$$

where $G$ is the the number of stress-bearing connections per unit of volume and $\tau$ is the typical lifetime of these connections. Since the density of connections in a polymer melt is mainly a function of the total molecular weight of the polymer, and depends to a lesser extent on the polymer structure, the viscosity should scale with the correlation time of the system. A good measure for the correlation time is the time of formation of the mesophase structure. For this reason the hexagonal phase is expected to be more viscous than the lamellar phase by at least an order of magnitude.

Experimental evidence here comes from two sources: from polymer systems and from surfactant rheology. First, for block copolymers it has been reported that the hexagonal phase is formed only under continuous shear with strain amplitude $\gamma = 600\%$, while the lamellar phase orders completely when a strain amplitude $\gamma = 5\%$ is applied. This difference indicates that the hexagonal phase is much more viscous than the lamellar phase. Qualitative results can be found in the literature on surfactant mesophases. In fact, the hexagonal phase was initially detected when studying the phase behavior of soaps, as this phase was responsible for the high viscosity and difficult processing conditions encountered in systems with certain composition and temperature ranges.

The comparison between our simulations and non-ionic surfactants is quantitatively correct, as both in experiment and simulation the viscosity ratio (or the ratio of formation times) between hexagonal and lamellar phase is roughly a factor of 10.

V. CONCLUSIONS

The conclusions that we can draw unambiguously from the present simulations are as follows.

- The length scale over which lamellar and hexagonal domains spontaneously order in our DPD simulations without shear compares well with the experiment.
- The hexagonal phase is formed from the disordered state via a connected tube phase.
- Hydrodynamic interactions play a dominant role in the formation of the hexagonal phase.
- The lamellar phase is formed from the disordered state avoiding the connected tube phase.
- The role of hydrodynamic interactions in the formation of the lamellar phase is marginal.
- For two $AB$ block copolymers of the same molecular weight but different $A$ to $B$ ratio, the lamellar phase is formed an order of magnitude faster than the hexagonal phase.

Our interpretation of the difference between the pathways towards hexagonal phase and lamellar phase is that the former is formed via a nucleation-and-growth mechanism, whereas the latter is formed via a spinodal decomposition mechanism. We speculate that the nucleation-and-growth mechanism is pertinent to the hexagonal phase formation because the intermediate connected tube phase resembles the gyroid phase, and is therefore metastable. The disordered lamellar structure does not form via such a metastable struc-
ture. Finally, from the different times of formation we infer a higher viscosity for the hexagonal phase than for the lamellar phase, which is in line with ample experimental evidence.

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40. R. G. Larson (private communication).